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SULFUR DIOXIDE CONVERSION UNDER CORONA DISCHARGE CATALYSIS

BY

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For

Division of Air Pollution
Bureau of State Services - EH
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ABSTRACT

Synthetic flue gas was exposed to ultraviolet radiation and to a corona discharge in laboratory type reactors and the efficiency of SO_2 oxidation to SO_3 for each of these methods was compared. For the conditions studied, corona treatment appeared to be superior to ultraviolet, showing efficiencies of 300 and 1470 cm^3 of the flue gas per watt hour for SO_2 conversions of 99.5 and 75%, respectively.

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1.0 Introduction

Air pollution problems, now nation-wide, are coming under study and discussion by state authorities. Many state legislatures have passed measures which establish quality standards for ambient air. Lack of adequate air cleaning processes has spurred development activity to find less costly methods than those presently available.

One of the principle offending materials is sulfur dioxide which arises from the use of low grade coals or oils in combustion processes. Efficient removal methods have been worked out for relatively high concentrations, however, when it is present in amounts less than 0.5% mass transfer effects are large and the usual absorption techniques quite inefficient.

Oxidation of the SO_2 to SO_3 would greatly simplify the problem since the latter is easily removed, even at low concentrations, due to its rapid hydrolysis on contact with moisture. Thermodynamically the reaction

$$SO_2 + 1/2\ O_2 = SO_3$$

is nearly complete at temperatures below 200 C. The equilibrium constant (1 atm.) falls rapidly with increasing temperature, as illustrated in Figure No. 1. Despite this the reaction rate is the factor that determines the practicability of a process and in this case the uncatalyzed rate is much too slow to be of any value.

A silent electrical discharge, or corona discharge, generates active chemical species such as excited molecules or free radicals. If oxygen atoms are formed by corona discharge in an oxygen containing atmosphere, such as flue gas, one would expect a reduction of the SO_2 content due to formation of SO_3.

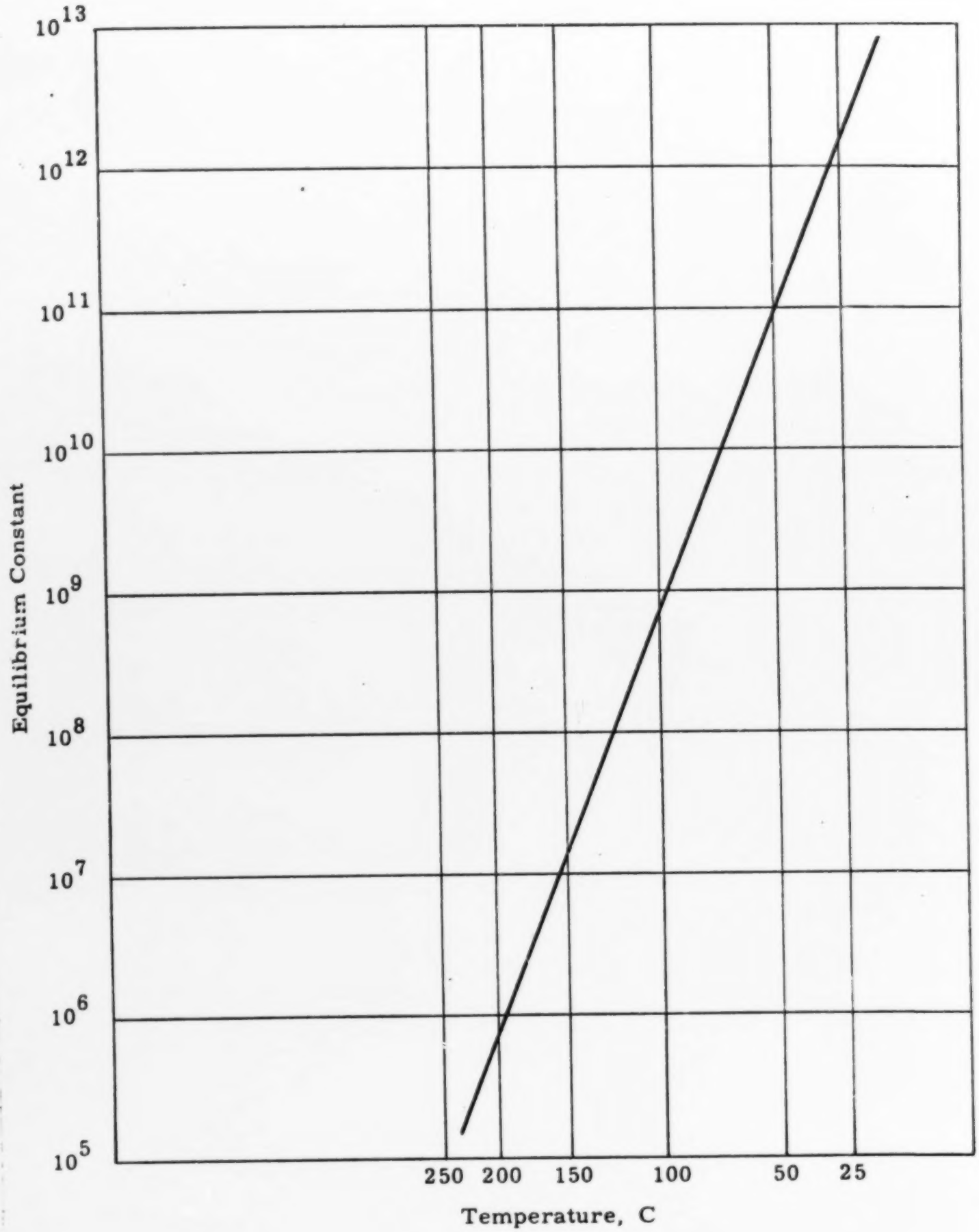


Figure 1. Variation of Equilibrium Constant with Temperature for the Reaction $SO_2 + 1/2\ O_2 = SO_3$.

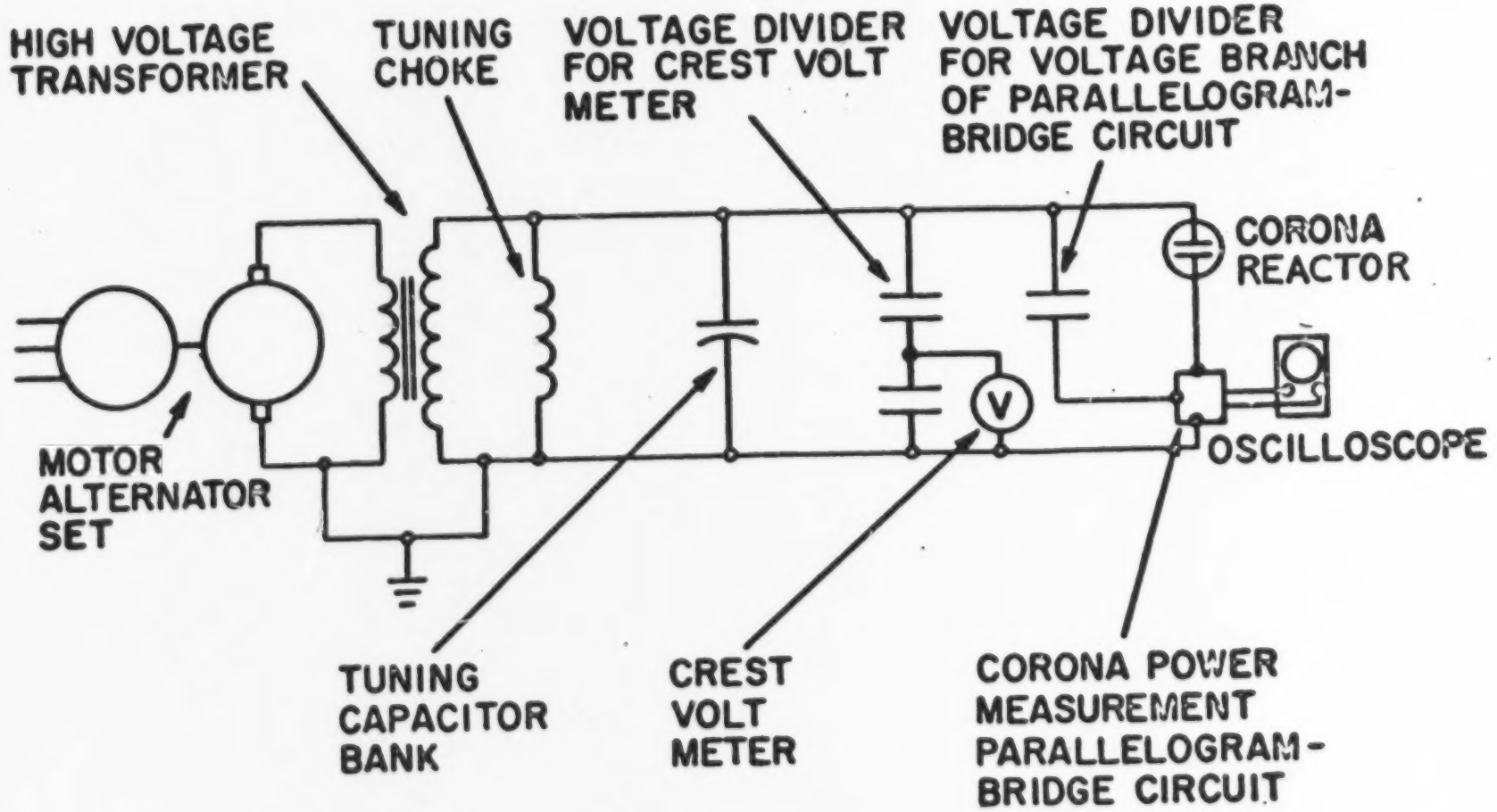
It is the purpose of this study to test the feasibility of converting the SO_2 in flue gas to SO_3 with a corona discharge and compare this approach with the photochemical conversion obtained from an ultraviolet radiation source.

2.0 Description of Apparatus

2.1 Generation and Measurement of Corona Power

The corona generating equipment consists of five major components: a high voltage interlocked cage for housing the test equipment; a device for converting low frequency power to high frequency power; a transformer to provide the required high voltage; a corona reaction cell; and instrumentation to permit measurement and control of the power supply, corona, and other critical electrical parameters. A motor-alternator generates the required voltage by varying the field winding of the 10,000 cycle alternator which feeds the primary of a high voltage transformer as shown in Figure No. 2. A choke and a capacitor bank are used in parallel with the corona reactor and present a "tuned circuit" to the transformer for efficient power utilization. The crest voltmeter indicates peak voltage rather than rms values as usually obtained from ordinary voltmeters. The oscilloscope displays the relationship between the voltage applied to the reactor electrodes and the charge flow in the circuit. Before corona occurs the oscilloscope figure is a slant line. As corona is initiated the slant line opens to a parallelogram figure, the area of which, after proper calibration, is directly related to the power dissipated in the reactor.

This technique for measuring corona power is a modification of an approach due to Manley (1) which has been used over the past twenty years. It dates back to early high voltage and corona oscillogram measurements which H. J. Ryan (2), and F. W. Peek, Jr. (3) reported about the turn of the last century.



BASIC POWER AND INSTRUMENTATION CIRCUIT

Figure 2

A bridge circuit, with separate "voltage" and "charge" branches utilizing capacitance voltage dividers feeds proportional signals to the X-Y axes of the oscilloscope. The X-Y product, then, is a measure of the energy per cycle dissipated in the cell. When multiplied by the frequency the result is total power.

It should be noted, however, that this approach to corona power measurement is an experimental, laboratory technique which should not be construed as having any specific production line tolerances and accuracy. There are many possible sources of error. These are:

1. The measurement of the high voltage applied to the cell, and the voltage axis calibration of the oscilloscope, as affected by the high voltage capacitance divider and the full scale tolerance of the high voltage voltmeter.
2. The determination of the charge flowing through the corona cell, which is affected by the tolerance of the capacitors in the "charge" branch of the bridge circuit and the charge axis calibration of the oscilloscope.
3. The accuracy of power supply frequency determination, since the frequency is a factor in the final calibration figure.
4. The determination of parallelogram area and shape. This is the greatest possible source of error. The shape and clarity of the parallelogram figure is affected by the steadiness of cell corona, and by the corona cell characteristics.

The area may be determined in several ways.

a. Photographing the parallelogram on the oscilloscope with a Polaroid camera and measuring the area with a planimeter, noting any scale factors involved.

b. Tracing the parallelogram area with wax pencil on a transparent film material and measuring the figure. This method provides a means of holding the wattage constant and noting any changes in the shape of the parallelogram.

c. Measuring the parallelogram directly with a flexible, transparent, centimeter scale.

Best accuracy is obtained with the largest parallelogram figure that can be completely contained on the oscilloscope.

Comparison of area estimates made by method c (above) on different oscilloscope ranges show that it is possible to get agreement on area estimates within ten percent. If the tolerances on all aspects of corona power measurement were to add up in the same direction, the error in measurement might be as great as twenty percent. A comparison of the parallelogram-oscilloscope technique with other methods of measuring corona power shows close agreement, and indicates that the probable error is more likely within fifteen percent.

A calorimetric check of corona power showed the parallelogram power measurement to be 17 percent lower than the calorimetric power.

A comparison of high voltage transformer primary power measurements made with a high frequency wattmeter, and secondary power measurements made with the parallelogram-oscilloscope technique (including provision for transformer losses) gave results agreeing within fifteen percent, with the parallelogram measurement being on the low side. A comparison of parallelogram power measurement method with power measurements made by a GE-ATL developed corona wattmeter showed agreement within 5 to 15 percent, with the parallelogram measurement once again on the low side. This pattern of low-side parallelogram power measurements probably indicates a tendency in this laboratory to be conservative in the measurement of parallelogram area.

2.2 Ultraviolet Reactor

The ultraviolet reactor was built around a General Electric Company, Model H1500-A23 lamp which is a quartz tubular type, 19-1/2 in. long, having a lighted length of 12 in. and a diameter of 1-1/8 in. It operates at a potential of 425 volts and requires a current of 3.9 amps. Table I shows the spectral distribution over the range of 2200 to 7600 Angstroms. Slightly less than 500 watts are radiated over the ultraviolet region; 189, 157, and 145 watts in the far, middle, and near ultraviolet regions, respectively.

The reactor assembly consisted of mounting this lamp axially in a pyrex jacket having an inside diameter of 2-1/8 in. The annular space between the jacket and the lamp served as the reaction zone with the gas entering at one end, traversing the length of the lamp and leaving at the other end.

2.3 Corona Reactor

The corona reactor, made of quartz, is illustrated in Figure No. 3. It consisted of two vertically mounted concentric cylinders fitted with standard taper attachments as shown. The corona generating portion of the reactor is the long straight section made up of the outer quartz tube, gas gap, and inner quartz tube. In operation, the feed material was introduced at the top of the reactor, passed down through the annular space between the two tubes, and leaves at the bottom. The central cylinder, closed off at the bottom, served as the high potential electrode. For the low temperature runs it was cooled with circulating water, and for the high temperature runs it was packed with steel wool. A conductive coating applied to the outside of the reactor, over the 11 in. section, served to define the corona zone and complete the electrical circuit by being tied to the ground. The electrode gap was 7.6 mm, its logarithmic mean cross-sectional area, 339 cm^2, and the gap volume, 128 cm^3.

TABLE I

Model H1500-A23 Lamp

Watts Radiated at Various Wavelength Bands

Wavelength Bands Angstroms	Watts	
2200-2300	18.017	
2300-2400	22.940	
2400-2500	21.823	Far ultraviolet
2500-2600	78.154	
2600-2700	39.027	
2700-2800	9.003	
2800-2900	27.556	
2900-3000	21.822	Middle ultraviolet
3000-3100	39.584	
3100-3200	67.954	
3200-3300	8.069	
3300-3400	13.346	
3400-3500	5.633	
3500-3600	4.619	Near ultraviolet
3600-3700	104.697	
3700-3800	3.451	
3800-4000	5.532	

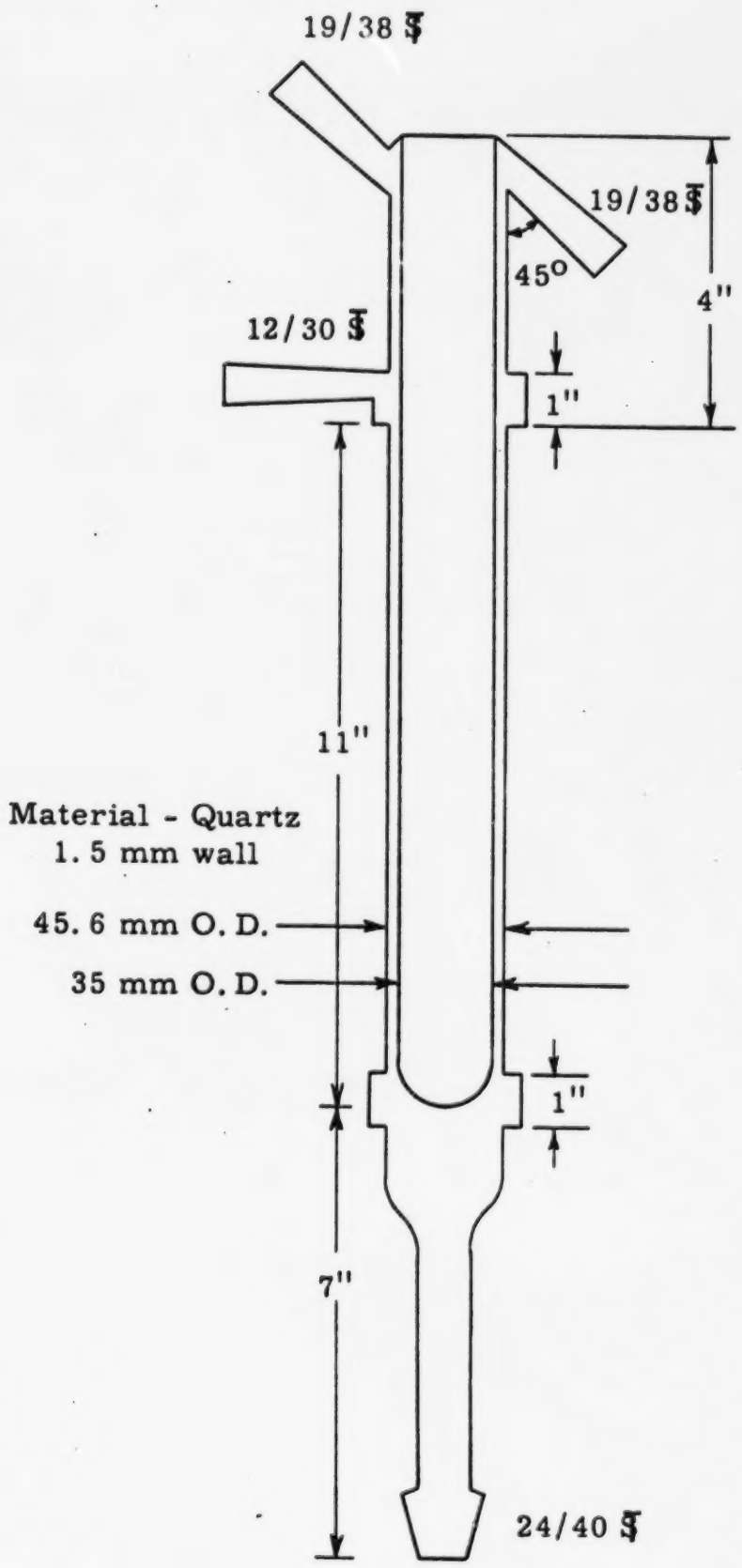


Figure 3. Falling Film Reactor

2.4 Reaction Train

The equipment was arranged as shown in Figure No. 4 with either the corona reactor or the ultraviolet reactor connected to the system.

Synthetic flue gas, at atmospheric pressure, was adjusted to contain 5.5% H_2O in the saturator by a method developed by Hawk, et al, at the Bureau of Mines (4). The water in the saturator can be vaporized at any desired rate by adjustment of the energy input to the heating element immersed in the water. Flue gas passing through the saturator carries with it water in an amount that is dependent on the rate of the vaporization; this rate being so regulated that the quantity of water introduced is in excess of that required by the test conditions. The gas-steam mixture then passes into a mixing tube which serves to break up the direction of gas flow, facilitating condensation of excess water and helping to equalize the final temperature of the gas. The apparatus was so adjusted that water vapor continuously condensed throughout the length of the tube, and, as the gas was always in contact with liquid water, the mixture leaving at the top of the apparatus consisted of gas saturated with water at the temperature measured at this point.

A heater between the gas saturator and the reactor was used to keep the gas above its dew point and raise the temperature of the gas prior to treatment in the reactor.

Treated gas passed out of the system through another heated section where the sample was withdrawn. The temperature in this section was maintained above the dew point to prevent loss of water and SO_3 from the gas sample being collected for analysis.

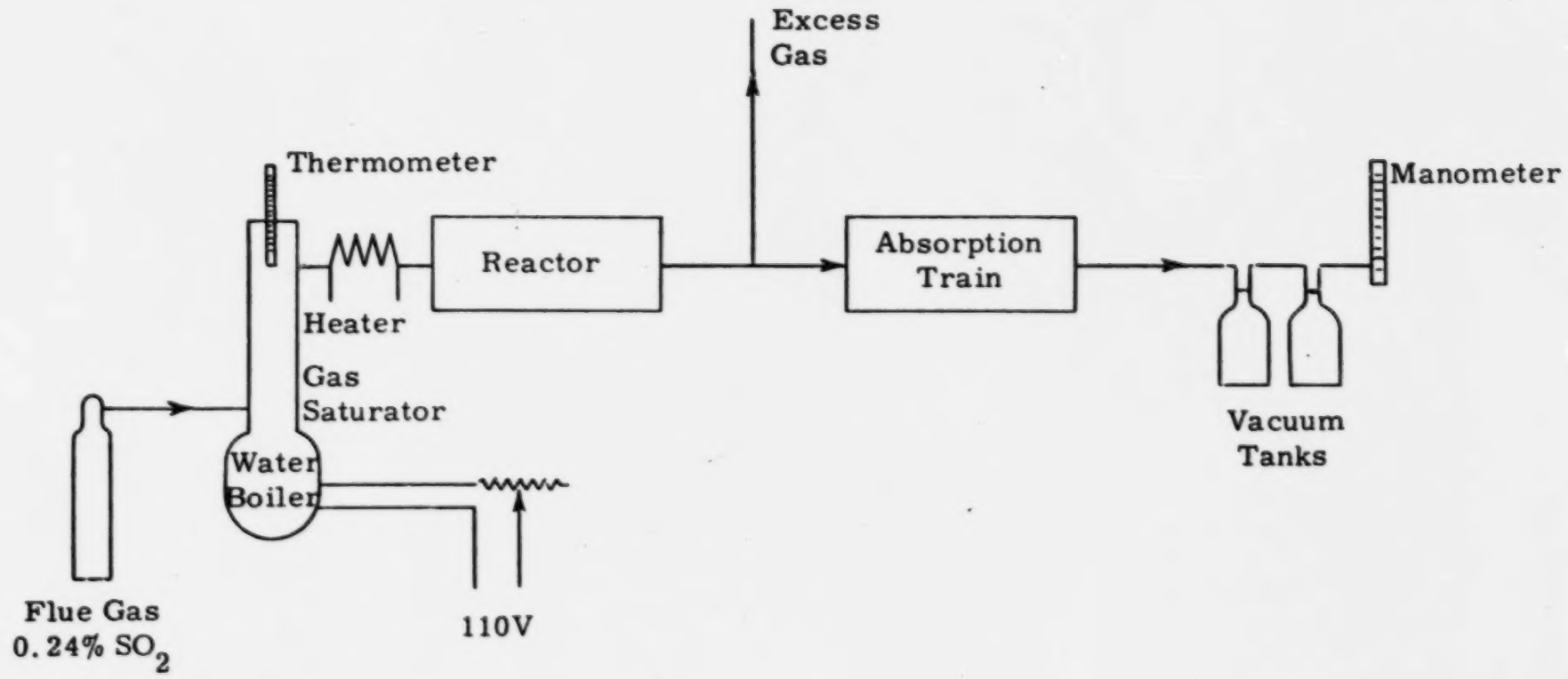


Figure 4. Arrangement of Equipment.

3.0 Experimental Procedure

3.1 Synthetic Flue Gas

A gas mixture having the approximate composition (dry basis):

CO_2	12.5%
O_2	6.5%
SO_2	0.25%
N_2	balance

was purchased from the Matheson Company, Inc., East Rutherford, New Jersey. Mass spectrographic analysis showed 13.0% CO_2, 4.0% O_2, and 82.5% N_2, a fair agreement with the composition specified. SO_2 concentration, determined by the Shell Development method (see section 3.3), was 0.27%.

3.2 Analytical Methods

Concentrations of sulfur dioxide and sulfur trioxide were determined by the "Shell Development Method" (5) using a calibrated vacuum tank system to draw the gas sample through the absorption train.

Concentrations of the oxides of nitrogen were determined by the phenoldisulfonic acid method of the "Air Pollution Control District, County of Los Angeles" (6).

3.3 Description of Runs

First the gas saturator was started and allowed to warm up, then the flue gas flow rate was brought up to the test value and the gas heater turned on. When the gas temperature stabilized (within 2 F of test values) the corona or ultraviolet was started. A gas sample was collected over a period of an hour at a flow rate of about .35 l/min.

At the conclusion of the sampling period the absorption train was blanked off from the reactor which then was shut down. After purging the absorption system the trapped gases were collected for analysis.

Blank runs were conducted in the above manner with identical flows and temperatures except that power was not applied to the reactor.

4.0 Results and Discussion

4.1 Ultraviolet Runs

Three runs were made using the ultraviolet reactor in place of the corona reactor. It appeared that the UV was not as effective at oxidizing SO_2 as the corona.

The feed gas which analyzed 2460 ppm SO_2 was passed through the reactor at 1.7 l/min. with no power applied and there was a decrease of 1685 ppm SO_2. With UV power and the same flow rate, a decrease of 1764 pp SO_2 was obtained. At a flow rate of 4.1 l/min. the decrease was 1665 ppm SO_2. The volume of flue gas treated per ultraviolet watt-hour was 200 and 492 cm^3, respectively (67 and 164 based upon total applied power of 1500 watts), for which the conversions were less than 75%. The data are shown in Table II.

4.2 Corona Runs

Corona treatment of synthetic flue gas converted sulfur dioxide to the trioxide in amounts proportional to the corona energy applied. As an aid in understanding the reactor performance it was desirable to establish a sulfur balance around the reactor. While the change in SO_2 concentration was of primary importance, a more complete understanding could be obtained from a knowledge of the SO_3 produced since this permitted an estimate of any elemental S formed. It was

TABLE II

ULTRAVIOLET TREATMENT OF FLUE GAS

Run	1	2	3
Feed Flow Rate, cm^3 $min.^{-1}$	1670	1670	4100
Reactor Feed Temperature, C	80	110	100
Reactor Outlet Temperature, C	130	155	260
Ultraviolet Contact Time, Min.	(.30)(1)	.30	.12
Sample Size, l	20.6	19.5	21.9
$BaCl_2$, m.e.	132.5	113.8	146.2
SO_2 Concentration in Effluent, ppm	775	696	795
SO_2 to SO_3 Conversion, % (2)	68.5	71.7	67.7
SO_2 Converted, cm^3/watt-hr (3)	-----	11.80	27.3
Flue Gas Treated, cm^3/watt-hr (3)	-----	66.8	164.
Flue Gas Treated, ft^3/watt-hr (3)	-----	.00236	.0058
Power Consumption KWH/ft^3	-----	.423	.173

Notes

(1) Power not applied
(2) Based on tank analysis
(3) Based on total applied power

not possible to obtain a consistent value of SO_3 concentration due to sample contamination problems which arose from a variety of circumstances. At first, the purging of the analytical train was conducted too close to the reactor outlet. Then fog and condensed moisture were drawn into the SO_3 absorber. Equipment alterations, and the addition of heaters to the sampling lines improved but did not eliminate the problem. A summary of these results follows:

CONCENTRATION OF SULFUR OXIDES

Run	Reported Concentration		Expected Concentration,
	ppm SO_2	ppm SO_3	ppm SO_3
Tank I	2686	-----	------
1	20	4144	2666
2	153	4520	2533
4	596	2323	2090
5	13	11200	2673
6	397	22500	2289
7	609	291	2077
Tank II	2420	-----	------
8	615	614	1805

Run #3 was conducted to show that these inconsistent SO_3 data were due to sampling techniques and not caused by the corona reactor. The run was performed under the same flow and temperature conditions as Runs #1 and #2 but the synthetic flue gas mixture was scrubbed with a solution of H_2O_2 to remove the SO_2 from the gas mixture before it entered the reactor. Without corona power the gas analyzed 6 ppm SO_2 and 6 ppm SO_3. With the power applied, the gas analyzed 15 ppm SO_2 and 6 ppm SO_3 from which it was concluded that it was not the reactor products that caused the erratic SO_3 values.

Table III shows the operating conditions for the corona runs along with the results obtained (based on SO_2 concentration). These data show that the conversion of SO_2 to SO_3 varies directly with the applied power and inversely with the flow rate, and that increasing the gas temperature from 50 to 140 C does not appear to have any great effect on the yield. The higher temperature lowers the gas breakdown potential about 5 KV and a more uniform corona discharge occurs at a considerably lower power level. Over the range of variables investigated, the volume of SO_2 converted per unit of applied energy varied directly with the gas rate (see Figure No. 5). At sufficiently high gas flow rates the conversion rate will approach some asymptotic value where the film gradients affecting mass transfer become negligible; in this feasibility study the reaction mechanism and kinetics were not explored. Many side reactions undoubtedly occur inasmuch as corona does not act on any specific molecule to the exclusion of the others. An indication of this is shown in the analysis for oxides of nitrogen which was conducted on the sample obtained from Run #9 and gave a yield of 1964 ppm calculated as NO_2.

Interspersed between the corona runs were 7 blank runs, experiments conducted under similar flow and temperature conditions but without the application of corona power. The sampling problems, mentioned before, were the same, with SO_3 being "held-up" in the system. The range of SO_2 values reported probably reflect the sampling error more than any changes in feed composition as the tank of synthetic gas mixture was consumed. Table IV lists the data for these runs.

TABLE III

CORONA TREATMENT OF FLUE GAS

Run No.	1	2	3(3)	4	5	6	7	8(1)	9(4)
Feed Flow Rate, cm^3 $min.^{-1}$	721	721	721	721	1670	4150	8780	1620	600
Reactor Energy, watt-hr.	363	237	273	147	330	329	359	194	229
Potential, K volts peak	15.0	14.1	15.3	13.7	14.8	14.7	14.6	10.1	11.1
Reactor Feed Temperature, C	---	---	130	119	95	67	70	130	160
Reactor Effluent Temperature, C	---	---	46	50	71	120	105	142	160
Reactor Electrode Temperature, C	20	20	20	20	20	20	20	390	400
Corona Contact Time, min.	.178	.178	.178	.178	.0766	.0308	.0146	.0792	.213
Sample Size, l	22.28	20.60	24.36	20.13	22.77	20.02	20.91	22.27	.8197
m.e. $BaCl_2$	.0375	.2625	.0125	1.4000	.0250	.6625	1.0562	1.1375	---
SO_2 Concentration in Effluent, ppm	20	153	6	596	13	397	609	615	---
SO_2 to SO_3 Conversion,(2) %	99.2	94.1	---	77.7	99.5	85.2	77.6	74.9	---
SO_2 Converted, cm^3/watt-hr.	31.8	46.2	---	61.5	81.1	173.2	305.	92.5	---
Flue Gas Treated, cm^3/watt-hr.	119	182	---	294	304	756	1468	501	---
Flue Gas Treated, ft^3/watt-hr.	.0042	.0064	---	.0104	.0107	.0268	.0519	.0177	---
Power Consumption, KWH/ft^3	.238	.155	---	.0963	.0934	.0374	.0193	.0394	---

NOTES:

(1) Feed gas changed between runs 7 and 8.

(2) Based on tank analysis.

(3) Feed gas scrubbed to remove SO_2.

(4) Sample analyzed 1964 ppm oxides of nitrogen.

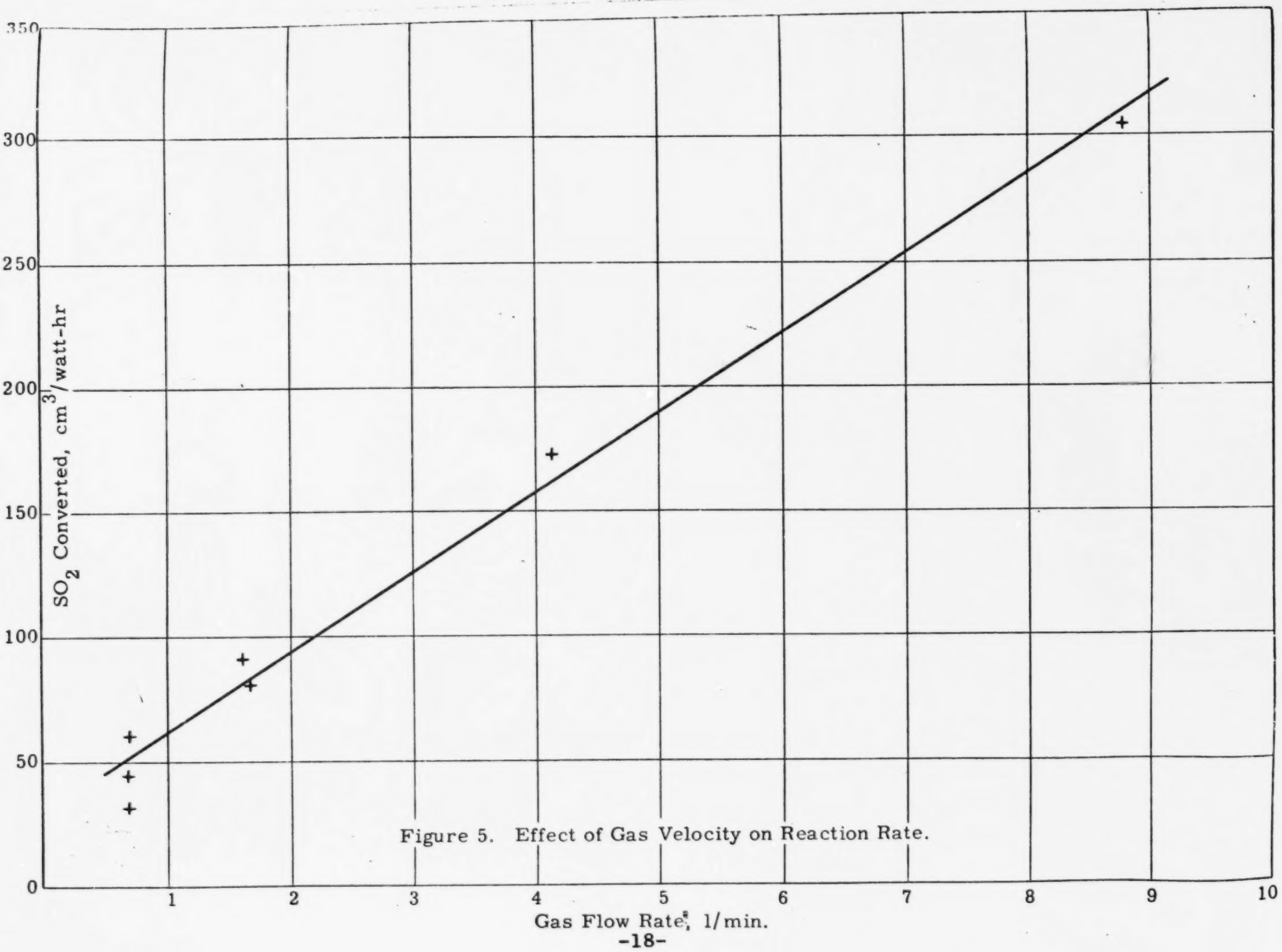


Figure 5. Effect of Gas Velocity on Reaction Rate.

TABLE IV

BLANK RUNS WITH FLUE GAS

Run	Sample Size, l	$BaCl_2$ m.e.	SO_2 Concn., ppm	$BaCl_2$ m.e.	SO_2 Concn., ppm
			Tank I		
1	26.09	6.0875	2686	-----	-------
2	21.39	3.7250	2086	1.6781	944
3	19.26	3.5375	2210	1.5688	980
4	23.70	2.3875	1212	.2000	102
			Tank II		
5	21.30	----	----	.0712	40
6	14.90	2.9925	2420	.0275	22
7	21.12	4.3375	2480	.0750	43

5.0 Summary

Synthetic flue gas was exposed to ultraviolet radiation and to a corona discharge in laboratory type reactors and the efficiency of SO_2 oxidation to SO_3 for each of these methods was compared. For the conditions studied, corona treatment appeared to be superior to ultraviolet, showing efficiencies of 300 and 1470 cm^3 of flue gas per watt hour for SO_2 conversions of 99.5 and 75% respectively.

While it was possible, in a corona discharge, to convert these substantial amounts of the sulfur dioxide, the energy required to accomplish the conversion appeared to be excessive. Thus, for the 99% reduction in SO_2 cited, 0.09 KWH/ft^3 of flue gas (90 KWH/1000 ft^3) was required and for 75% reduction, 0.04 KWH/ft^3 (40 KWH/1000 ft^3). Assuming that 10,000 cps power was available at one cent per KWH, the electrical energy cost would be \$0.90 and \$0.40 per 1000 ft^3 for the two examples.

Although not proven conclusively, it seems plausible that much of the corona energy supplied to the system was wasted by attack on water vapor and nitrogen. This problem would be amplified in an actual flue gas where attack on unburned hydrocarbons would represent additional energy losses.

It is suggested that the external corona generation of ozone which could then be injected into the flue gas stream, as proposed by Hall and Wintermate (7,8) might overcome these difficulties since; (1) corona generation of ozone in clean, dry oxygen or air proceeds with relatively high efficiency and (2) ozone would be expected to attack SO_2 more preferentially.

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